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(54) Title: HYDROGENATED AROMATIC POLYMER COMPOSITIONS CONTAINING STABILIZERS

(57) Abstract

The present invention is a polymer compositions comprising: a) a hydrogenated aromatic polymer; b) a benzofuranone; and c) a hindered phenol. The composition of the present invention can be processed at high temperatures without losing significant Mw and thus can produce molded articles having excellent physical properties.

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HYDROGENATED AROMATIC POLYMER COMPOSITIONS CONTAINING STABILIZERS

This invention relates to hydrogenated aromatic polymer compositions. This invention particularly relates to molded products produced from hydrogenated aromatic polymer compositions.

Hydrogenated aromatic polymers such as polycyclohexylethylene (PCHE) have been used as a replacement for polycarbonates. PCHE has the advantage of good transparency, heat resistance and low moisture absorbency. In the production of PCHE and the formation of molded articles, the polymer is typically processed at temperatures of from 230 to 350°C. However, when PCHE is processed at such temperatures, the molecular weight of the polymer greatly decreases and the physical properties of the polymer and subsequently produced molded article severely declines. JP2586575 by Mitsubishi attempts to solve this problem by adding a hindered phenol and phosphorus type heat stabilizers. However, although this combination decreases the amount of polymer degradation which occurs, the polymer still loses significant Mw and thus physical properties.

Therefore, there remains a need to develop a hydrogenated aromatic polymer composition which will not lose significant Mw upon processing at 230 to 350°C and will produce an molded article having excellent physical properties.

In one aspect, the present invention is a polymer composition comprising:

a) a hydrogenated aromatic polymer and a heat stabilizer mixture consisting essentially of:

b) a benzofuranone, and

c) a hindered phenol.

In another aspect, the present invention is a molded article produced from such a polymer composition .

The composition of the present invention can be processed at high temperatures without losing significant Mw and thus can produce molded articles having excellent physical properties.

In one embodiment, the present invention is a polymer composition comprising a hydrogenated aromatic polymer and a stabilizer composition. The hydrogenated aromatic polymer used in the present invention includes any aromatic polymer which has been hydrogenated to a level of at least 60 percent aromatic hydrogenation, generally at least 80 percent, preferably at least 90 percent, more preferably at least 95 percent and most preferably at least 98 percent. Methods of

hydrogenating aromatic polymers are well known in the art such as that described in US-A-5,612,422 by Hahn and Hucul, herein incorporated by reference, wherein aromatic polymers are hydrogenated by contacting an aromatic polymer with a hydrogenating agent in the presence of a silica supported metal hydrogenation catalyst having a narrow pore size distribution and large pores.

Aromatic polymers which are hydrogenated by such processes include any polymeric material containing pendant aromatic functionality. Pendant aromatic functionality refers to a structure wherein the aromatic group is a substituent on the polymer backbone and not embedded therein. Preferred aromatic groups are C_{6-20} aryl groups, especially phenyl. These polymers may also contain other olefinic groups in addition to the aromatic groups. Preferably, the polymer is derived from a monomer of the formula:

$$\begin{array}{c} \mathrm{R'} \\ | \\ \mathrm{Ar{-}C{-}CH_2} \end{array}$$

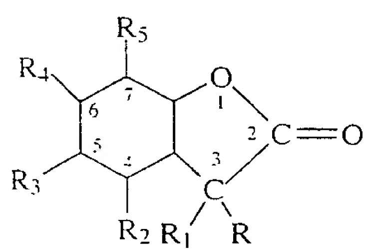
wherein R' is hydrogen or alkyl, Ar is phenyl, halophenyl, alkylphenyl, alkylhalophenyl, naphthyl, pyridinyl, or anthracenyl, wherein any alkyl group contains 1 to 6 carbon atoms which may be mono or multisubstituted with functional groups such as halo, nitro, amino, cyano, carbonyl and carboxyl. More preferably Ar is phenyl or alkyl phenyl with phenyl being most preferred. Typical vinyl aromatic monomers which can be used include styrene, alpha-methylstyrene, all isomers of vinyl toluene, especially paravinyltoluene, all isomers of ethyl styrene, propyl styrene, vinyl biphenyl, vinyl naphthalene, and vinyl anthracene, and mixtures thereof. Homopolymers may have any stereostructure including syndiotactic, isotactic or atactic; however, atactic polymers are preferred. In addition, hydrogenated copolymers containing these aromatic monomers including random, pseudo random, block and grafted copolymers may be used in accordance with the present invention. For example, copolymers of vinyl aromatic monomers and comonomers selected from nitriles, acrylates, acids, ethylene, propylene, maleic anhydride, maleimides, vinyl acetate, and vinyl chloride may also be used such as styrene-acrylonitrile, styrene-alpha-methylstyrene and styrene-ethylene. Hydrogenated block copolymers of vinyl aromatic monomers and conjugated dienes such as butadiene, isoprene may also be used. Examples include styrene-butadiene, styrene-isoprene, styrene-butadiene-styrene and styrene-isoprene-styrene copolymers. Further examples of block copolymers may be found in US-A-4,845,173, US-A-4,096,203, US-A-4,200,718, US-A-4,210,729, US-A-4,205,016, US-A-3,652,516, US-A-3,734,973,

US-A-3,390,207, US-A-3,231,635, and US-A-3,030,346. Blends of such hydrogenated polymers with other polymers including impact modified, grafted rubber containing hydrogenated aromatic polymers may also be used. Preferably, the hydrogenated aromatic polymer is polycyclohexylethylene (PCHE) prepared by hydrogenating atactic polystyrene.

The weight average molecular weight (Mw)of the hydrogenated aromatic polymer is typically from 1,000, generally from 20,000, preferably from 50,000, more preferably from 100,000 and most preferably from 200,000 to 400,000, preferably to 375,000, more preferably to 350,000 and most preferably to 325,000.

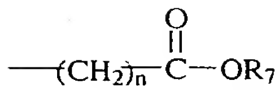
To maintain the Mw and thus the excellent physical properties of the hydrogenated aromatic polymer, a stabilizer combination has been discovered which prevents polymer degradation during processing at high temperatures such as temperatures up to 350°C. The stabilizer combination consists of a benzofuranone and a hindered phenol. The benzofuranone can be produced by reacting an aminomethyl substituted phenol or a halomethyl substituted phenol with an ionic cyanide compound, hydrolyzing the product thereof, followed by ring closure condensation. Typical benzofuranones and methods of producing are described in US-A-4,325,863.

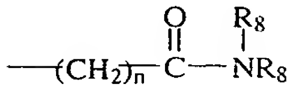
The benzofuranone used in the composition of the present invention is preferably of the formula:

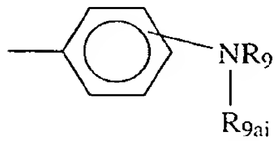


in which either

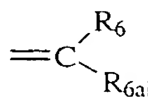
R is hydrogen, and R_1 is hydrogen; C_{1-22} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl, C_5 or C_6 cycloalkyl; phenyl; phenyl substituted by one to three substituents selected from the group consisting of C_{1-12} alkyl, hydroxy, C_{1-12} alkoxy, C_{1-18} acyloxy, chloro or nitro, with the provisos that: (1) when the phenyl ring contains more than one C_{1-12} alkyl group, said alkyl groups contain a maximum of 18 carbon atoms, (2) the maximum number of hydroxy substituents is two, and (3) the maximum number of each of the substituents selected from C_{1-12} alkoxy, C_{1-18} acyloxy, chloro and nitro is one; or a group of formula (a/4), (a/5) or (a/6)

 (a/4)

 (a/5)

 (a/6)

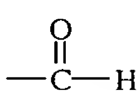
or R and R_1 together form a group (a/2)

 (a/2)

either

each of R_2 to R_5, independently, is hydrogen; C_{1-12} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl-C_5 or C_6 cycloalkyl; C_{1-22} alkoxy; phenoxy; phenoxy substituted by one or two C_{1-12} alkyl groups,

said alkyl groups having a maximum of 16 carbon atoms; C_{1-18} acyloxy; chloro; phenyl-C_{1-9} alkyl; phenylthio; phenyl-C_{1-9} alkyl or phenylthio substituted on the phenyl ring by one to three substituents selected from C_{1-12} alkyl, hydroxy and R_{15}CO—O—; phenyl; phenyl substituted by one or two C_{1-12} alkyl groups, said alkyl groups having a maximum of 16 carbon atoms; nitro; 2-furanylcarbonyloxy; 2-thienylcarbonyloxy; a group of formula (b/2), (b/3) or (b/4)

 (b/2)

$$-CH_2-S-R_{12} \qquad (b/3)$$

$$-CH(C_6H_5)CO-O-R_7 \quad \text{or:} \qquad (b/4)$$

a group of formula (a/4) or (a/5) as defined above;

with the provisos that:

(a) a maximum of two of R_2 through R_5 is C_5 or C_6 cycloalkyl, C_{1-5} alkyl; C_5 or C_6 cycloalkyl, C_{1-22} alkoxy, phenoxy, substituted phenoxy, C_{1-18} acyloxy or chloro; and

(b) a maximum of one of R_2 through R_5 is optionally substituted phenyl, phenyl-C_{1-9} alkyl or phenylthio, nitro, 2-furanylcarbonyloxy, 2-thienylcarbonyloxy or a group of formula (b/2), (b/3), (b/4), (a/4) or (a/5), provided that only the R_3 substituent can be a group of formula (b/3) or (b/4) and only the R_3 or R_5 substituent can be a group of formula (a/5);

or R_2 and R_3, together, form a condensed benzene ring,

or R_3 and R_4, together, form a furan(2) one ring in which the 3-position bears the substituents R and R_1 as defined above,

or R_4 and R_5, together, form tetramethylene or a furan(2) one ring in which the 3-position bears the substituents R and R_1 as defined above,

and one of the two remaining substituents is hydrogen and the other is any one of the significances given for R_2 to R_5 above;

either

R_6 is C_{1-18} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl; C_5 or C_6 cycloalkyl; benzyl; $(C_6H_5)_2CH$; phenyl; phenyl mono- or disubstituted by C_{1-12} alkyl, provided that when the phenyl ring contains more than one C_{1-12} alkyl group, said alkyl groups contain a maximum of 16 carbon atoms; phenyl monosubstituted by hydroxy; phenyl mono- or disubstituted by methoxy; phenyl monosubstituted by chloro; phenyl monosubstituted by dimethylamino; 3,5-di-tertiary butyl-4-hydroxyphenyl; b -naphthyl; pyridinyl; 2-furyl; or a group of formula (c/1) or (c/2)

$$-\overset{\overset{\displaystyle O}{\|}}{C}-OR_7 \qquad \text{(c/1)}$$

$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R_8}{|}}{N}-R_8, \text{ and} \qquad \text{(c/2)}$$

R_{6a} is hydrogen; C_{1-18} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl; C_5 or C_6 cycloalkyl; phenyl or benzyl;

or

R_6 and R_{6a}, together with the carbon atom to which they are bound, form an unsubstituted 5- or 6-membered aliphatic ring or a 5- or 6-membered aliphatic ring monosubstituted by C_{1-4} alkyl;

each

R_7, independently, is hydrogen; C_{1-18} alkyl; alkyl-O-alkylene having a maximum of 18 carbon atoms; alkyl-S-alkylene having a maximum of 18 carbon atoms; di-C_{1-4} alkylamino-C_{1-8} alkyl; C_{5-7} cycloalkyl; phenyl; or phenyl substituted by one to three

C_{1-12} alkyl groups, said alkyl groups having a maximum of 18 carbon atoms;

either

each R_8, independently, is hydrogen; C_{1-18} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl-C_5 or C_6 cycloalkyl; phenyl; phenyl substituted by one or two C_{1-12} alkyl groups, said alkyl groups having a maximum of 16 carbon atoms; or a group of formula (d/1), (d/2) or (d/3)

$$—CH_2CH_2OH \qquad (d/1)$$

$$—CH_2CH_2OC_{1\text{-}18}alkyl \qquad (d/2)$$

$$—CH_2CH_2—O—\overset{O}{\overset{\|}{C}}—R_{11}; \qquad (d/3)$$

or both

R_8's, together with the nitrogen atom, form an unsubstituted piperidine or morpholine ring;

R_9 has one of the significances of R_8;

R_{9a} is hydrogen; C_{1-18} alkyl; or a group of formula (d/1), (d/2) or (d/3) as defined above;

R_{11} is hydrogen; C_{1-22} alkyl; C_{5-7} cycloalkyl; phenyl; phenyl-C_{1-6} alkyl; or phenyl or phenyl-C_{1-6} alkyl substituted on the phenyl ring by one or two C_{1-12} alkyl groups, said alkyl groups having a maximum of 16 carbon atoms;

R_{12} is C_{1-18} alkyl; 2-hydroxyethyl; phenyl; or C_{1-9} alkylphenyl;

R_{15} is C_{1-22} alkyl or phenyl;

and n is 0, 1 or 2.

R is preferably hydrogen.

R_1 is preferably R_1', where R_1' is hydrogen; C_{1-18}alkyl; phenyl optionally substituted by one or two C_{1-8}alkyl groups and/or a hydroxyl group; (a/4) or (a/5) or together with R is (a/2). More preferably R_1 is R_1'', where R_1'' is C_{1-18}alkyl, or phenyl optionally substituted by one or two C_{1-8}alkyl groups and/or a hydroxyl group. Most preferably R_1 is phenyl optionally substituted by C_{1-4}alkyl.

When R_1 is optionally substituted phenyl, such phenyl preferably bears no chlorine atom. When R_1 as substituted phenyl bears a hydroxyl group said hydroxyl group is preferably adjacent to a branched alkyl group such as tert.-butyl, more preferably located between two such groups.

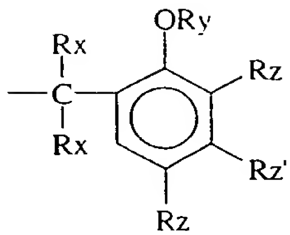
When R_1 is phenyl substituted by an acyloxy group preferably such group is in the 2- or 4-position and preferably a C_{1-4}alkyl group is also present especially in para position to the acyloxy group.

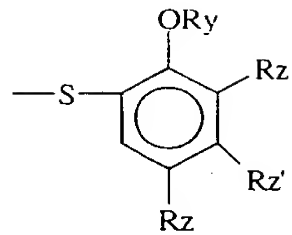
When R_1 is optionally substituted phenyl, R_2 is preferably hydrogen or methyl, more preferably hydrogen.

When any two of R_2 to R_5 form a condensed benzene ring, tetramethylene or a condensed furan(2)one ring as defined above preferably both the other substituents are hydrogen or one is hydrogen and the other is C_{1-4}alkyl or COOH, most preferably both are hydrogen.

When anyone of R_2 to R_5 is phenylalkyl or phenylthio in which the phenyl nucleus is substituted as defined above, preferably said phenylalkyl or phenylthio group is R_3 or R_5, more preferably R_5.

Furthermore, when such substituent is present as R_3 preferably R_2 and R_4 are hydrogen and R_5 is hydrogen or alkyl (pref. C_{1-5}) and when such a substituent is present as R_5, preferably R_2 and R_4 are hydrogen and R_3 is hydrogen or alkyl (pref. C_{1-8} especially tert. octyl). Preferred phenylalkyl or phenylthio groups in the case of R_5 are those in which the phenyl nucleus has a hydroxy or R_{15} CO—O—substituent in ortho position to the alkyl or thio group. Preferred such groups are:


(PA)


(PT)

in which

each R_X, independently, is hydrogen or (C_{1-4})-alkyl,

R_Y is hydrogen or $CO\text{-}R_{15}$, and

each R_Z, independently, is hydrogen, C_{1-9}-alkyl (linear or branched) and

R_Z' is hydrogen or C_{1-4} linear alkyl.

In the group (PA) preferably each R_X, independently, is hydrogen or C_{1-4}alkyl, more preferably hydrogen or methyl; each R_Z independently, is preferably hydrogen or C_{1-4}alkyl more preferably hydrogen, methyl or tert. butyl with hydrogen or methyl being most preferred. R_Z' is preferably hydrogen or methyl, most preferably hydrogen. In the group (PT) each R_Z, independently, is preferably hydrogen or (C_{1-8})alkyl, more preferably, the R_Z ortho to OR_Y is hydrogen and the other tert. octyl. R_Z' is preferably hydrogen.

R_2 is preferably R_2', wherein R_2' is hydrogen, (C_{1-4})alkyl or together with R_3' forms a condensed benzene ring. More preferably R_2 is R_2', where R_2' is hydrogen or methyl, especially hydrogen.

R_3 is preferably R_3', where R_3' is hydrogen, C_{1-12}alkyl, phenyl, C_{1-18}alkoxy, phenoxy, C_{1-18}alkylcarbonyloxy, (a/**4**), (a/**5**), (b/**2**), (b/**4**) or together with R_2' forms a condensed benzene ring or together with R_4' forms a furan(**2**)one nucleus in which R is hydrogen and R_1 is preferably R_1. More preferably R_3 is R_3'', where R_3'' is hydrogen, (C_{1-12})alkyl, phenyl, (a/**4**) or together with R_2' forms a condensed benzene ring. Even more preferably R_3 is R_3''', where R_3''' is hydrogen, (C_{1-9})alkyl or (a/**4**). Most preferably R_3 is R_3'''', where R_3'''' is hydrogen or alkyl C_{1-9}(preferably C_{1-5}), with methyl, tert.-butyl or tert.-amyl being most preferred.

When R_3' forms a furanone ring together with R_4' the oxygen atom of said nucleus is preferably bound to the R_4' position. When R_3 is (b/**2**) and R_{11} is other than hydrogen the adjacent hydroxyl group is preferably in the **6**-position.

R_4 is preferably R_4', where R_4' is hydrogen, C_{1-12}alkyl, C_{1-18}alkoxy, phenoxy or

together with R_3' or R_5' forms a furan(2)one ring in which R is hydrogen and R_1 is preferably R_1 or R_4' together with R_5' forms tetramethylene. More preferably R_4'' is R_4'', where R_4 is hydrogen, C_{1-12}alkyl, C_{1-18}alkoxy or phenoxy. Even more preferably R_4 is R_4''', where R_4''' is hydrogen or C_{1-12}alkyl, especially hydrogen. The preferred alkyl groups as R_4 are C_{1-8}alkyl, more preferably C_{1-4}, with methyl and tert.-butyl being the most preferred alkyl groups.

When R_4' together with R_5' forms a furan(2)one nucleus the oxygen atom of said nucleus is preferably bound to the 7-position.

R_5 is preferably R_5', where R_5' is hydrogen, C_{1-12}alkyl, phenyl, (a/4), (a/5), (PA), (PT) or together with R_4' forms tetramethylene or a furan(2)one ring. More preferably R_5 is R_5'', where R_5'' is hydrogen, C_{1-12}alkyl, (PA) or (PT). More preferably R_5 is R_5''', where R_5''' is hydrogen or C_{1-8}alkyl with alkyl, preferably C_{1-5}alkyl, being most preferred. The preferred C_{1-5}alkyl groups are methyl, tert.-butyl and tert.-amyl.

When a furan(2)one nucleus is formed by any two of R_3' to R_5' preferably the R_1's are the same. Most preferably they are phenyl.

When R_6 is substituted phenyl, such phenyl is preferably hydroxyphenyl, phenyl substituted by up to two C_{1-12}alkyl groups with max. 16 carbon atoms in the combined substituents or 3,5-di-tert.-butyl-4-hydroxyphenyl; more preferably any substituted phenyl as R_6 is mono substituted by one C_{1-12}-alkyl group or is 3,5-di-tert.-butyl-4-hydroxyphenyl. Preferably any phenyl as R_6 is unsubstituted. Any alkyl as R_6, preferably contains 1 to 12, more preferably 1 to 8, most preferably 1 to 4 carbon atoms.

R_6 is preferably R_6', where R_6' is C_{1-18}alkyl, phenyl, 3,5-di-tert.-butyl-4-hydroxyphenyl, (c/1) or together with R_{6a} is cyclohexylidene. More preferably R_6 is R_6'', where R_6'' is C_{1-12}alkyl, phenyl, 3,5-di-tert.-butyl-4-hydroxyphenyl or together with R_{6a} and the common C-atom form cyclohexylidene. Most preferably R_6 is R_6''', where R_6''' is C_{1-12}alkyl or phenyl.

Any alkyl as R_{6a} preferably contains 1 to 12, more preferably 1 to 8, most preferably 1 to 4 carbon atoms, especially methyl.

R_{6a} is preferably R_{6a}', where R_{6a}' is hydrogen, C_{1-12}-alkyl or together with R_6 and the common C-atom forms cyclohexylidene. Most preferably R_{6a} is hydrogen.

When R_6 is substituted phenyl or $CH(C_6H_5)_2$ or (c/1) R_{6a} is preferably hydrogen.

R_7 is preferably R_7', where R_7' is hydrogen, C_{1-18}alkyl, phenyl optionally substituted by up to two C_{1-12}alkyl groups with max. 16 carbon atoms in the combined substituents. More preferably R_7 is R_7'', where R_7'' is C_{1-18}alkyl, phenyl or C_{1-12}alkylphenyl. Most preferably R_7 is C_{1-18}alkyl, especially C_{8-18}alkyl.

Each R_8, independently, is preferably R_8', where R_8' is hydrogen, C_{1-18}alkyl or both R_8' together with the N-atom form piperidine. More preferably each R_8, independently is hydrogen or C_{1-18}alkyl. Preferred alkyl groups as R_8 are C_{1-12}—, preferably C_{1-8}—, most preferably C_{1-4}alkyl.

R_9 is preferably R_9', where R_9' is hydrogen, C_{1-8}alkyl or (d/1). More preferably R_9 is hydrogen or C_{1-8}alkyl. Any alkyl as R_9 preferably contains 1 to 8, more preferably 1 to 4 carbon atoms.

R_{9a} is preferably R_{9a}', where R_{9a}' is hydrogen, C_{1-6}—alkyl or (d/1). Any alkyl as R_{9a} preferably contains 1 to 8, more preferably 1 to 4 carbon atoms.

R_{11} is preferably R_{11}', where R_{11}' is hydrogen, C_{1-18}alkyl or phenyl. R_{11} in (b/2) is preferably phenyl.

Any alkyl as R_{11} preferably contain 4 to 17 carbon atoms.

R_{12} is preferably R_{12}', where R_{12}' is C_{1-12}alkyl, phenyl or 4-(alkyl C_{1-9})phenyl.

n in (a/4) or (a/5) as R_1 is preferably 1.

n in (a/4) or (a/5) as R_5 is preferably 1.

n in (a/4) or (a/5) as R_3 is preferably 2.

The preferred cycloalkyl groups are cyclohexyl and methylcyclohexyl, especially cyclohexyl.

Preferred compounds of formula I_C are those in which R_1 is R_1',R_2 is R_2', R_3 is R_3', R_4 is R_4', and R_5 is R_5' .More preferred compounds are those where R is hydrogen, R_1 is R_1'', R_2 is R_2'', especially hydrogen, R_3 is R_3'', preferably R_3''', R_4 is R_4'' and R_5 is R_5''. Especially preferred are those compounds where R is hydrogen, R_1 is C_{1-4}alkyl substituted phenyl, or phenyl, especially phenyl, R_2 is hydrogen, R_3 is R_3'''', R_4 is hydrogen and R_5 is R_5''' especially C_{1-5}alkyl.

In preferred embodiment R_1 is C_{1-18} alkyl, phenyl or phenyl substituted by one to three substituents selected from C_{1-8} alkyl and hydroxy, with the proviso that the

maximum number of C_{1-8} alkyl substituents is two and the maximum number of hydroxy substituents is one.

In a most preferred embodiment, the benzofuranone is 5,7-di-t-butyl-3-(3,4-di-methylphenyl)-3H-benzofuran-2-one(CAS No. 181314-48-7).

The benzofuranone is advantageously present in amounts of from 10, generally from 20, typically from 30, preferably from 50, more preferably from 100 and most preferably from 200 ppm to 4000, generally to 2000, typically to 1000, preferably to 800, more preferably to 600 and most preferably to 400 ppm, based on the weight of the hydrogenated aromatic polymer.

The hindered phenol used in the composition of the present invention can be any sterically hindered phenol which will act as a heat stabilizer for the hydrogenated aromatic polymer composition. Typical hindered phenols include: tetrakis[methylene(3,5-di-tert-butylhydroxyhydrocinnamate)]methane, β-(4-hydroxy-3,5-ditert.-butylphenyl)-propionicacidstearylester, tetrakis[methylene-3(3',5'-ditert-butyl-4-hydroxyphenyl)-propionate]-methane, 1,3,3-tris(2-methyl-4-hydroxy-5-tert.-butylphenyl)-butane,1,3,5-tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, bis(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-dithiolterephthalate, tris(3,5-ditert.-butyl-4-hydroxybenzylisocyanurate, triester of 3,5-di-tert.-butyl-4-hydroxyhydrocinnamic acid with 1,3,5-tris-(2-hydroxyethyl)-s-triazin-2,4,6-(1H,3H,5H)-trione, bis[3,3-bis-4'hydroxy-3-tert-butylphenyl)-butaneacid]-glycolester, 1,3,5-trimethyl-2,4,6-tris-(3,5-ditert-butyl-4-hydroxybenzyl)-benzene, 2,2'methylenebis(4-methyl-6-tert-butylphenyl)terephthalate, 4,4-methylene-bis-(2,6-ditert-butylphenol), 4,4'-butylidene-bis(6-tert-butyl-meta-cresol), 4,4-thio-bis(2-tert-butyl-5-methylphenol), 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) and octadecyl- 3,5-di-tert-butyl-4-hydroxyhydrocinnamate.

Hindered phenols are advantageously present in the composition of the present invention in amounts of from 0.01, generally from 0.03, typically from 0.05, preferably from 0.1, more preferably from 0.15 and most preferably from 0.20 to 1, generally to 0.8, typically to 0.6, preferably to 0.5, more preferably to 0.4 and most preferably to 0.3 wt. percent based on the weight of the hydrogenated aromatic polymer.

Generally, the ratio of the benzofuranone to the hindered phenol is 99:1 to 1:99. Typically, the ratio is 75:25 to 25:75, preferably 50:50 to 25:75, more preferably 20:80 to 10:90, and most preferably 15:85.

The stabilizers can be combined with the hydrogenated aromatic polymer by any conventional method. The stabilizers can be pre-mixed prior to addition to the polymer or each component can be individually added to the polymer The stabilizers can be dry blended with pellets of hydrogenated aromatic polymer, but are preferably dissolved in the polymer and more preferably mixed with hydrogenated polymer prior to devolatilization and pelletization..

Other additives may be present in the composition of the invention as long as the heat stability is not further modified. Typical additives include viscosity modifiers such as mineral oil and low Mw hydrogenated vinyl aromatic polymers and hydrogenated copolymers of styrene, α-methyl styrene, vinyl toluene, and/or indene, mold release additives, and UV stabilizers.

The composition comprising the hydrogenated aromatic polymer and the stabilizers can be used to produce optical media such as optical media discs. Methods of molding discs are well known in the art as described in <u>The Compact Disc Handbook</u>, 2nd edition, by Pohlmann, and include compression and injection molding. Typically, the molding temperature is between 200 and 400°C, and is preferably between 260 and 350°C. Optical media discs are useful as optical high density information recording medium such as compact discs, video discs, DVD discs, CD-rewritable discs, memory discs for computers, optical magnetic discs or optical cards.

The molded articles produced have excellent physical properties including flexural strength, tensile strength, and impact properties.

The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and they should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

<u>EXAMPLE 1</u>

A stabilizer composition containing 85 weight percent octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate powder and 15 weight percent 5,7-di-t-butyl-3-(3,4-di-methylphenyl)-3H-benzofuran-2-one powder is prepared by mixing the two powders. The stabilizer mixture is then added to polycyclohexylethylene polymer pellets having a Mw of 249,000 in an amount of 0.2 parts per hundred resin (pph) based on the weight of the polymer. The polymer and stabilizer mixture is mixed by shake blending the components in a bag. The shake blended mixture is then emptied into a twin screw extruder hopper. The extruder temperature profile is

configured such that zones 1-3 and the die heater are all at 260°C. The screw speed is set to 60 rpm. The polymer mixture is extruded into strands, cooled in a water bath, pelletized and collected in a bag. The collected pellets are then emptied into the hopper for another extruder pass and the process is repeated for a total of four passes. A sample of a strand is taken near the end of each pass prior to pelletization, from which molecular weight results are determined. Molecular weight determinations are made using gel permeation chromatography (GPC) analysis. Results are listed in Table I.

COMPARATIVE EXAMPLE

The procedure of Example 1 is followed except that 0.5 pph of octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate is added to the PCHE polymer. Results are listed in Table I.

TABLE I

Extruder Pass	0.2 pph Stabilizer mixture (Mw)	0.5 pph hindered phenol* (Mw)
0	249,000	249,000
1	249,800	243,800
2	240,100	226,700
3	231,500	220,100
4	225,100	213,600

*Comparative Example

The composition containing the combination of stabilizers of benzofuranone and hindered phenol prevents polymer degradation much more efficiently than when a hindered phenol is used alone.

EXAMPLE 2

The procedure of Example 1 is repeated with the stabilizers as listed in Table II.

TABLE II

		Mw for Extruder Pass				
Sample	Stabilizer	0	1	2	3	4
1	0.17% Irganox® 1076 + .03% Irganox®HP136		249.8	240.1	231.5	225.1
2*	None	249	152.9	130.4	112.1	101.6
3*	0.2% Irganox® 3114[a]		192.8	159.7	142.1	126.8
4*	0.2% Irganox® 1330[b]		223.9	199.9	190	171.7
5*	0.2% Irganox® 1076[c]		235.8	201.7	192.4	175.7
6*	0.2% Irganox®1010[d]		238.8	213.7	197.5	190
7*	0.2% Irgafos® 168[e]		228.4	168.7	146.8	121.3
8*	0.2% Irganox®HP 136[f]		228.9	203	189.1	174.8
9*	0.1% Irganox® 1076 + .1% Irgafos® 168		226.9	190.2	170.9	151.9
10*	.085% Irganox® 1076 phenol + .085% Irgafos® 168 phosphite + .03% Irganox®HP136 lactone		241.9	228.4	217	208.5
11*	0.5% Irganox® 1076		243.8	226.7	220.1	213.6

[a]Irganox® 3114 is 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione.

[b]Irganox® 1330 is 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene.

[c]Irganox® 1076 is octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate.

[d]Irganox®1010 is tetrakis[methylene(3,5-di-tert-butylhydroxyhydrocinnamate)]methane.

[e]Irgafos® 168 is tris(2,4-di-tert-butylphenyl)phosphite.

[f]Irganox®HP 136 is 5,7-di-t-butyl-3-(3,4-di-methylphenyl)-3H-benzofuran-2-one.

*Comparative Examples

The composition of the present invention is clearly superior in Mw when compared to compositions containing other heat stabilizers.

CLAIMS:

1. A composition comprising:

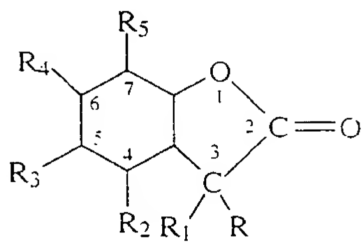
a) a hydrogenated aromatic polymer,

b) a benzofuranone, and

c) a hindered phenol.

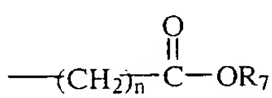
2. The composition of Claim 1 wherein the hydrogenated aromatic polymer is polycyclohexylethylene.

3. The composition of Claim 1 wherein the benzofuranone is of the formula:

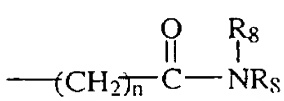


in which either

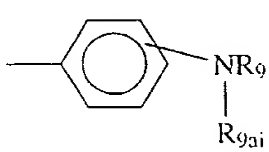
R is hydrogen, and R_1 is hydrogen; C_{1-22} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl, C_5 or C_6 cycloalkyl; phenyl; phenyl substituted by one to three substituents selected from the group consisting of C_{1-12} alkyl, hydroxy, C_{1-12} alkoxy, C_{1-18} acyloxy, chloro or nitro, with the provisos that: (1) when the phenyl ring contains more than one C_{1-12} alkyl group, said alkyl groups contain a maximum of 18 carbon atoms, (2) the maximum number of hydroxy substituents is two, and (3) the maximum number of each of the substituents selected from C_{1-12} alkoxy, C_{1-18} acyloxy, chloro and nitro is one; or a group of formula (a/4), (a/5) or (a/6)



(a/4)



(a/5)



(a/6)

or R and R_1 together form a group (a/2)

$$=C\begin{matrix}\diagup R_6 \\ \diagdown R_{6ai}\end{matrix} \qquad (a/2)$$

either

each of R_2 to R_5, independently, is hydrogen; C_{1-12} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl-C_5 or C_6 cycloalkyl; C_{1-22} alkoxy; phenoxy; phenoxy substituted by one or two C_{1-12} alkyl groups,

said alkyl groups having a maximum of 16 carbon atoms; C_{1-18} acyloxy; chloro; phenyl-C_{1-9} alkyl; phenylthio; phenyl-C_{1-9} alkyl or phenylthio substituted on the phenyl ring by one to three substituents selected from C_{1-12} alkyl, hydroxy and R_{15}CO—O—; phenyl; phenyl substituted by one or two C_{1-12} alkyl groups, said alkyl groups having a maximum of 16 carbon atoms; nitro; 2-furanylcarbonyloxy; 2-thienylcarbonyloxy; a group of formula (b/2), (b/3) or (b/4)

$$-\overset{\overset{\displaystyle O}{\|}}{C}-H \qquad (b/2)$$

$$-CH_2-S-R_{12} \qquad (b/3)$$

$$-CH(C_6H_5)CO-O-R_7 \quad \text{or;} \qquad (b/4)$$

a group of formula (a/4) or (a/5) as defined above;

with the provisos that:

(a) a maximum of two of R_2 through R_5 is C_5 or C_6 cycloalkyl, C_{1-5} alkyl; C_5 or C_6 cycloalkyl, C_{1-22} alkoxy, phenoxy, substituted phenoxy, C_{1-18} acyloxy or chloro; and

(b) a maximum of one of R_2 through R_5 is optionally substituted phenyl, phenyl-C_{1-9} alkyl or phenylthio, nitro, 2-furanylcarbonyloxy, 2-thienylcarbonyloxy or a group of formula (b/2), (b/3), (b/4), (a/4) or (a/5), provided that only the R_3 substituent can be a group of formula (b/3) or (b/4) and only the R_3 or R_5 substituent can be a group of formula (a/5);

or R_2 and R_3, together, form a condensed benzene ring,

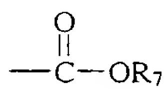
or R_3 and R_4, together, form a furan(2) one ring in which the 3-position bears the substituents R and R_1 as defined above,

or R_4 and R_5, together, form tetramethylene or a furan(2) one ring in which the 3-position bears the substituents R and R_1 as defined above,

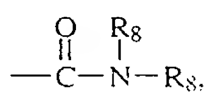
and one of the two remaining substituents is hydrogen and the other is any one of the significances given for R_2 to R_5 above;

either

R_6 is C_{1-18} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl; C_5 or C_6 cycloalkyl; benzyl; $(C_6H_5)_2CH$; phenyl; phenyl mono- or disubstituted by C_{1-12} alkyl, provided that when the phenyl ring contains more than one C_{1-12} alkyl group, said alkyl groups contain a maximum of 16 carbon atoms; phenyl monosubstituted by hydroxy; phenyl mono- or disubstituted by methoxy; phenyl monosubstituted by chloro; phenyl monosubstituted by dimethylamino; 3,5-di-tertiary butyl-4-hydroxyphenyl; b -naphthyl; pyridinyl; 2-furyl; or a group of formula (c/1) or (c/2)



(c/1)



and (c/2)

R_{6a} is hydrogen; C_{1-18} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl; C_5 or C_6 cycloalkyl; phenyl or benzyl;

or

R_6 and R_{6a}, together with the carbon atom to which they are bound, form an unsubstituted 5- or 6-membered aliphatic ring or a 5- or 6-membered aliphatic ring monosubstituted by C_{1-4} alkyl;

each

R_7, independently, is hydrogen; C_{1-18} alkyl; alkyl-O-alkylene having a maximum of 18 carbon atoms; alkyl-S-alkylene having a maximum of 18 carbon atoms; di-C_{1-4} alkylamino-C_{1-8} alkyl; C_{5-7} cycloalkyl; phenyl; or phenyl substituted by one to three

C_{1-12} alkyl groups, said alkyl groups having a maximum of 18 carbon atoms;

either

each R_8, independently, is hydrogen; C_{1-18} alkyl; C_5 or C_6 cycloalkyl; C_{1-5} alkyl-C_5 or C_6 cycloalkyl; phenyl; phenyl substituted by one or two C_{1-12} alkyl groups, said alkyl groups having a maximum of 16 carbon atoms; or a group of formula (d/1), (d/2) or (d/3)

$$—CH_2CH_2OH \qquad (d/1)$$

$$—CH_2CH_2OC_{1-18}alkyl \qquad (d/2)$$

$$—CH_2CH_2—O—\overset{\overset{\displaystyle O}{\|}}{C}—R_{11}; \qquad (d/3)$$

or both

R_8's, together with the nitrogen atom, form an unsubstituted piperidine or morpholine ring;

R_9 has one of the significances of R_8;

R_{9a} is hydrogen; C_{1-18} alkyl; or a group of formula (d/1), (d/2) or (d/3) as defined above;

R_{11} is hydrogen; C_{1-22} alkyl; C_{5-7} cycloalkyl; phenyl; phenyl-C_{1-6}alkyl; or phenyl or phenyl-C_{1-6} alkyl substituted on the phenyl ring by one or two C_{1-12} alkyl groups, said alkyl groups having a maximum of 16 carbon atoms;

R_{12} is C_{1-18} alkyl; 2-hydroxyethyl; phenyl; or C_{1-9} alkylphenyl;

R_{15} is C_{1-22} alkyl or phenyl;

and n is 0, 1 or 2.

4. The composition of Claim 1 wherein the benzofuranone is 5,7-di-t-butyl-3-(3,4-di-methylphenyl)-3H-benzofuran-2-one).

5. The composition of Claim 1 wherein component b) is present in an amount of 10 to 4000 ppm based on the weight of the hydrogenated aromatic polymer.

6. The composition of Claim 1 wherein component b) is present in an amount of 20 to 2000 ppm based on the weight of the hydrogenated aromatic polymer.

7. The composition of Claim 1 wherein component c) is octadecyl- 3,5-di-tert-butyl-4-hydroxyhydrocinnamate or tetrakis[methylene(3,5-di-tert-butylhydroxyhydrocinnamate)]methane.

8. The composition of Claim 1 wherein component c) is present in an amount of 0.01 to 1 wt. percent based on the hydrogenated aromatic polymer.

9. The composition of Claim 1 wherein component c) is present in an amount of 0.03 to 0.8 wt. percent based on the hydrogenated aromatic polymer.

10. The composition of Claim 1 wherein the ratio of component b) to component c) is from 10:90 to 20:80.

11. A molded article prepared from any of the compositions of Claim 1 through Claim 10.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/00189

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/15 C08K5/13 C08L23/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 335 (C-384), 13 November 1986 & JP 61 138648 A (MITSUI PETROCHEM IND LTD), 26 June 1986 see abstract ---	1,11

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 May 1999	27/05/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Engel, S

International Application No
PCT/US 99/00189

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 077 (C-0688), 14 February 1990 & JP 01 294753 A (MITSUBISHI KASEI CORP), 28 November 1989 cited in the application see abstract -& DATABASE WPI Section Ch, Week 9002 Derwent Publications Ltd., London, GB; Class A14, AN 90-013040 XP002102770 & JP 01 294753 A see abstract	1,11
A	EP 0 415 887 A (CIBA) 6 March 1991 see page 5, paragraph 1 - paragraph 2 see page 7, line 18 - line 31; claims 1,12; example 6	1,7
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